THE KINETICS OF THE REACTION OF STEAM ON POROUS CARBON TUBES

BY

DONALD STRONG SCOTT

B.Sc., University of Alberta, 1944
M.Sc., University of Alberta, 1946

ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF ILLINOIS, 1949

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INTRODUCTION

Although a considerable amount of work has been published on the kinetics of the reaction between steam and carbon, little has been accomplished in a general quantitative manner. A promising theory of the fundamental reaction mechanism has been outlined in recent publications (1), (2), (3), (4), and this work offers a confirmation of this theory and an extension of its applicability to a wider range of conditions.

The uncertainties concerning flow conditions, temperatures, heat transfer and concentration distribution which are always present in a packed bed type of reactor, were minimized in this investigation by employing a tubular reactor, the tube being composed of graphite. With this type of apparatus, the above difficulties are greatly reduced, and in particular, a much closer approach to true isothermal conditions is possible. In addition, the length of the reaction zone may be varied at will because of its geometrical uniformity, and thus facilitate a study of the differential changes occurring during the reaction.

Reaction rates and product compositions have been measured for a variety of conditions. Equations were derived from which reaction rate constants may be determined, and it is shown that the rate expression proposed will reproduce the observed data over a wider range of conditions than has been possible in the past.

THEORY

An expression for the rate of reaction between steam and carbon has been derived by Long and Sykes (4). This equation is of the form

$$\text{Rate} = \frac{k_1 p_1}{1 + k_2 p_2 + k_3 p_1}$$

where p_1 and p_2 are the partial pressures of steam and hydrogen, respectively, and the constants k_1, k_2, and k_3 are related to the rate constants of the individual steps of the proposed reaction mechanism.

By the assumption of a rate expression of the above form, integrated equations have been derived from which the rate constants

may be calculated with a small amount of experimental data. Two cases have been considered; first, that in which the water gas reaction occurs to only a small extent, and, secondly, the case where the water gas reaction approaches equilibrium. Assumptions made in these derivations are estimated to cause an error not exceeding 10% for molal conversions of steam up to 40%.

It is suggested that for higher conversions of steam the total rate of reaction may be expressed by the sum of the rates of the steam-carbon and carbon dioxide-carbon reactions, where each is measured in the absence of the other. Arguments are given in support of this supposition.

EXPERIMENTAL

The reactor consisted of a stainless steel tube into which a section of "National" graphite pipe, 1-inch inside diameter with a 3/16-inch wall thickness was placed. A tight fit was made between the steel tube and graphite pipe so that flow occurred only inside the pipe. Temperatures were measured by thermocouples in contact with the stainless steel shell.

Reaction products were analyzed by absorption in suitable reagents and weighing.

RESULTS AND CONCLUSIONS

Measurements of initial unsteady state changes suggest that the reaction mechanism occurring in the oxidation of graphite by steam is the same as that proposed for charcoal and steam (3) (4).

It was found that all reaction rates increased as the graphite tube was consumed, the relationship between the reaction rates and the average fraction of graphite present which had been consumed being logarithmic in nature for fractional consumptions up to at least 15%. This may be explained by the creation of new surface and new active centers as the graphite is consumed.

Reaction rate constants at two temperatures were calculated. The order of magnitude obtained, and the variation of these constants with temperature agree with recent work (4). The rate constants were shown to be independent of the flow velocity, indicating that mass diffusion is not a factor in determining the speed of reaction at these conditions.

Calculated and observed reaction velocities for the case in which the water gas reaction approaches equilibrium agree within 20% for a range of steam decompositions from 15% to 40%. The dif-

ferences are of the order of 5% at higher temperatures and low flow rates. The agreement can be improved by the addition of the rate of the carbon dioxide-carbon reaction to the calculated values. The discrepancies at low conversions can be explained in terms of uneven distribution of active centers along the reaction zone caused by a decreasing amount of oxidation of the graphite in this direction, and by the high degree of retardation of the reaction by the hydrogen produced.

The tubular reactor employed has given a good degree of temperature control with relatively simple experimental equipment, and reproducible data have been obtained.

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VITA

The author was born in Edmonton, Alberta, Canada, December 17, 1922, and received his elementary education in city and country schools of the Province of Alberta, graduating from Victoria High School in Edmonton in 1940. That year he entered the University of Alberta and in 1944 received the degree of Bachelor of Science in Chemical Engineering. After spending a year with Imperial Oil Limited in the petroleum engineering department of the Canol Project at Norman Wells, N. W. T., he returned to the University of Alberta and received the degree of Master of Science in Chemistry in 1946. The following fourteen months he was employed as a chemical engineer in the fermentations pilot plant of the Division of Applied Biology of the National Research Council of Canada in their Ottawa, Ontario, laboratories. In 1947 he was awarded a National Research Council of Canada Special Scholarship and the same year entered the University of Illinois. The following year the author was a University of Illinois Fellow in Chemistry.

The author has been a contributor to two publications appearing in the Canadian Journal of Research, Section F, Volume 26, November, 1948, under the titles "Production and Properties of 2,3-Butanediol XXVIII" and "Production and Properties of 2,3-Butanediol XXIX."

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